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Usage of nanoporous alumina in film temperature sensors

MICRO- AND NANOELECTRONICS -- MICRO- AND NANOSENSORS

Abstract

The effect of the anodic current density, temperature and concentration of the oxalic acid on the volume expansion of porous alumina films formed from 1.8 μm thick aluminum films has been investigated. Experiments showed that the volume expansion factor as well as the cell dimensions is proportional to the anodizing voltage. The dependence of the volume expansion factor (k) on the anodizing voltage (U) has the linear nature. The volume expansion factor in the 4% solution of oxalic acid can be defined by the following equation: $k = 1.092 + 0.007 \cdot U$. It was established, that the dependence of the logarithm of the ion current density on the inverse volume expansion factor of porous alumina has the linear nature. The possibility of integration porous anodizing of aluminum and copper electro-/electroless deposition techniques in the context of temperature sensor developing is also presented.

1. Introduction

Progress in electronic technologies and such advantages as small dimensions and weight, high thermosensitivity have resulted in rapid development of a new type of sensors-film temperature sensors. The main problem of manufacturing of film temperature sensors is a mutual co-ordination between elastic properties of thermosensitive material and protecting insulating coating. This problem can be solved by using nanoporous alumina as a material for protecting insulating coating in film temperature sensors. Films of porous alumina with a high regularity of the cell-porous structure are widely used for nanostructures in the electronic, magnetic and photon devices [1-3]. An important feature of nanoporous alumina is a low elastic modulus of about 90-140 GPa comparing with the value of 340-380 GPa for non-porous alumina [20,21].This feature allows to reduce mechanical stresses arising in film structures at cycle heating and cool-

ing. Thus, the long-term stability of electric characteristics of such film sensors is improved.

One of the most important parameters that determine film thickness as well as current density, electrolyte temperature and anodizing time is the volume expansion factor. The volume expansion factor is the ratio of the volume of the anodic Al oxide to the volume of Al consumed. It depends on the dissolution rate at the oxide/electrolyte interface and on the incorporation of acid anions and OH^- [4]. A barrier layer and walls of pores were established to be two-layered for porous films formed in the aqueous solutions of oxalic acid [5-7]. About 90 % of the structure is the outer layer, which contains Al oxide and anions of the electrolyte; the other 10 % is the inner layer, which consists of relatively pure Al oxide. Acid anion incorporation increases with current density and results in the increase of the volume of the porous oxide. The oxalate content in anodic oxide does not exceed the level of 2.4 wt. % [8]. As it is known for porous alumina formation the volume expansion of Al, which depends on anodizing regimes, can vary from 0.8 to 1.7 during an oxidation process [9]. Such a wide rate of change cannot be explained only by acid anion incorporation into the oxide film. Therefore, the main reason of such variation of the volume expansion factor of oxide films is a different field-assisted dissolution rate at the oxide/electrolyte interface [10].

Parameter spread, a variety of conditions for porous alumina formation as well as the problems at definition of the volume expansion factor (k) make it difficult to find general regularities. An interesting conclusion can be found in [11]. It was determined that for self-organized pore growth a dependence of the volume expansion of the aluminum during oxide formation on the anodizing voltage is systematic.

Thus, the aim of this work was to study the influence of current density, anodizing voltage and electrolyte temperature on the volume expansion factor in oxalic acid and to determine the interaction between these anodizing parameters. A mechanical profiler with a computer signal processing was used for these studies. Also SEM study of film structures and resistivity measurements were carried out.

The deposited thin films of aluminum can be used for studies of the volume expansion of the aluminum during oxidation. In this case all samples have the same thickness and morphology of the Al films. That is why using the step height between the aluminum surface and the porous alumina surface at the edge of the anodized region for through oxide formation the volume expansion can be calculated. Note that as a result of porous alumina formation the aluminum surface at the bottom of alumina has a

regular scalloped microstructure [4, 12]. Such a surface microstructure containing metal ridges and troughs provides a high value of conductivity of the Al layer even at small film thickness. This promotes good homogeneity of the oxidation onto an insulating substrate of the following type: oxide-coated silicon wafer or glass ceramic substrate [12, 13].

Electrochemical deposited copper was used as a thermosensitive material in film sensors. Electrochemical deposition of Cu provided high purity of films and so, high reproducibility of reproducibility of measurements.

The Cu lines in studied film sensors were built in nanoporous alumina. For that we used the processes of formation of trenches in alumina using a local etching and then, vacuum deposition of the barrier layer of Ta and filling of trenches by electroless and electrochemical deposition of Cu. The Ta layers have good adhesion properties on dielectric substrates and are often used as barrier layers for Cu interconnect metallization [22].

Cu temperature sensors with area of 2x5 mm and greater, electric resistance of 50 Ohm and protecting dielectric based on nanoporous alumina were manufactured. The electric characteristics of film sensors were studied in the temperature range of -60 to 160°C.

2. Experiment

2.1 Preparation of samples

Vapor deposition of aluminum films. Thin films of aluminum were used for investigations. The 1.8 μm thick films onto insulating glass ceramic substrates of 6.0 cm×4.8 cm size were formed by the vacuum deposition of 99.9% pure aluminum in the chamber of electron-beam evaporation «Oratorio-9» with the planetary rotation of substrates. The following regime of the aluminum deposition was used: the temperature of substrates is 413 ±20 K, the deposition rate is 3 $nm \cdot s^{-1}$, residual vacuum chamber pressure is 7.0 $\times 10^{-4}$ Pa. The thickness control of aluminum films during the vacuum deposition was carried out with the help of the quartz sensor. For the purposes of thickness measurement of the deposited Al film the step between the aluminum surface and the substrate surface was formed by chemical etching (mixed solution: phosphoric acid is 80 ml, nitric acid is 5 ml, water is 20 ml, temperature of etching is 40°Ñ) using a photoresist mask (Fig.1).

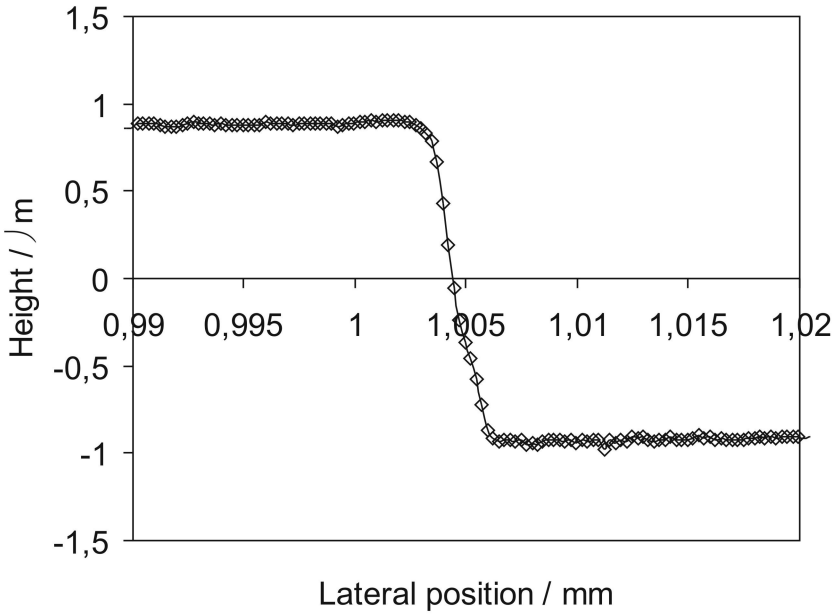

Fig.1. Step between the aluminum film surface and the surface of the substrate formed by chemical etching.

Mask formation for local porous anodizing. Samples with porous alumina with the area of 0.75 cm $\times$ 0.75 cm were made using a barrier Al oxide as the mask. Application of barrier Al oxide, instead of photoresist mask, prevents the mask damage and allows to form a local area of porous oxide with the reproduced and controlled size. It also ensures high accuracy of maintenance of the current density during porous anodizing. The formation of barrier Al oxide was carried out in the 1 % aqueous solution of citric acid by applying a photoresist mask. The process of anodizing was conducted in the combined electrical regime. The first stage consisted of anodizing at the potentiodynamic regime with a scanning rate of voltage (from 0.5 $V \cdot s^{-1}$ to 55 V). The second stage was at the potentiostatic regime of 5 minute duration at 55 V. It is necessary to use the formation voltage bigger than the voltage for porous anodizing for providing a stable masking. That is why the formation voltage of 55 V was applied. After removing the photoresist the substrate was divided into separate samples. Each of them contained a segment of aluminum film with the area of 0.5625 cm^2 for the subsequent porous anodizing.

Formation of porous alumina film. The process of porous anodizing was carried out in a double-electrode temperature-controlled glass cell with the tantalum cathode

(volume of the electrolyte was about 3 liters). We used a potentiostat/galvanostat (P5827M) as an electrochemical power supply. The galvanostatic anodizing regime with electrolyte stirring over the range of current densities from 1.62 to 4.8 mÀ·cm^{-2} was used to form porous alumina. It takes more than one hour for the anodizing process at the current densities smaller than 1.62 mÀ·cm^{-2}. Therefore, the effect of chemical dissolution of porous alumina becomes more noticeable and results in errors at definition of the volume expansion. On the other hand, it takes less than 15 minutes for the anodizing process at the current densities more than 4.8 mÀ·cm^{-2}. Such a short period of time makes it difficult to define the steady-state region of anodizing because of the close position to the initial non-steady state region. The 2%, 4% and 8 % aqueous solutions of oxalic acid were used as electrolytes. The temperature of the electrolyte during Al anodizing was 16°, 18° and 20°Ñ with the precision of ±0.2°Ñ. The anodizing time of the Al film down to the substrate was determined by a voltage jump seen on the kinetic dependence. This jump indicated that through anodizing was finished.

2.2 Copper thin film interconnections formation

Local dissolution of alumina layer. To deposit thin films of copper it was necessary to etch trenches in alumina layer. This was realized by means of local chemical dissolution of anodic Al oxide.

Local electrodeposition of copper thin films. Copper thin film conductors were formed by electroless and electrochemical deposition on tantalum adhesion underlayer.

As trenches in nanoporous alumina were formed, thin layer of Al_2O_3 (100-400 nm) was then sputtered and patterned to protect pores of porous alumina films. To obtain an adhesion between copper and substrate surfaces a thin adhesion layer of tantalum (50-70 nm) was sputtered to trenches' bottoms and walls. After that tantalum surfaces of trenches was activated by etching of tantalum surface oxide by substrate dipping in 1% hydrofluoric acid water solution for about 3-4 s.

Immediately after that seed copper layer was formed on Ta underlayer by electroless copper deposition (Fig. 2). Copper was deposited from a copper sulphate bath that includes also formaldehyde as reducing agent, EDTA as complexing agent for ions of copper and surfactant (RE-610). Deposition solution temperature of 60°C and pH 12.7 were kept constant.

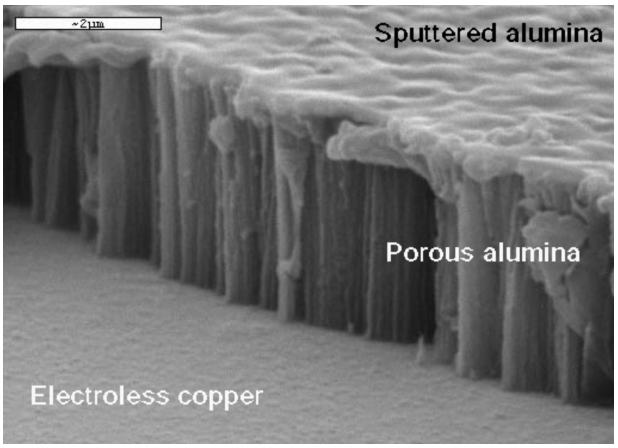

Fig. 2. A SEM image of trench after copper electroless deposition

Hereupon trenches with copper seed layer were filled by copper electroplating. Copper was plated from a bath that includes $CuSO_4 \cdot 5H_2O$ (200-240 g/L) and H_2SO_4 (50-70 g/L). Deposition solution temperature (20°C) and cathodic current density (1.5 A/dm^2) were kept constant. To prevent overfilling of trenches plating was stopped immediately as potential exceeds about 140 - 150% of its beginning value.

Finally, wet etching of sputtered protective layer of Al_2O_3 was realized to open pores of porous alumina films.

3. Results

3.1 Influence of anodizing regimes on the volume expansion factor

Fig. 3 shows the volume expansion factor (k) versus the anodizing voltage in the steady-state growth region of the porous alumina film as a function of temperature.

The obtained results show that the volume expansion factor of porous alumina films formed in oxalic acid depends on anodizing regimes, and in the range of the current density of 1.6-4.8 $mA \cdot cm^{-2}$ changes from 1.25 to 1.42.

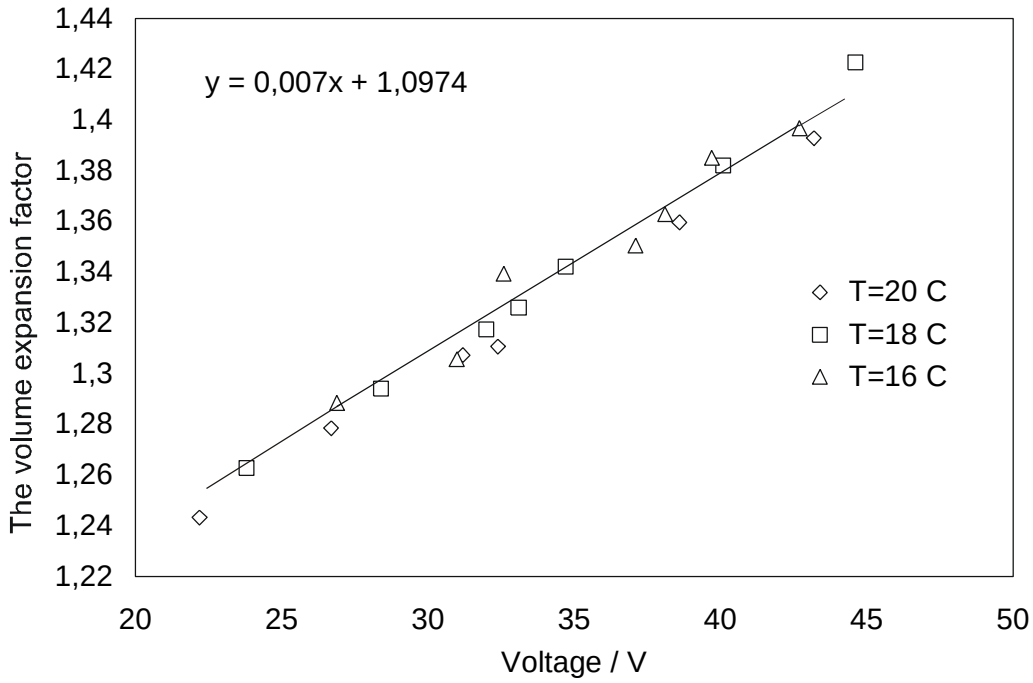

Fig. 3. Volume expansion factor (k) vs. the anodizing voltage in the steady-state growth region of the porous alumina film as a function of temperature (4 % solution of oxalic acid at the temperature of 16°, 18° and 20°C).

Referring to Fig. 4, the anodic current density, the concentration and the temperature of the electrolyte essentially influence the volume expansion of aluminum during oxidation. With anodizing at the constant current density, the increase of the electrolyte temperature decreases the anodizing voltage and the volume expansion factor. Meanwhile the increase of the current density increases above parameters. The increase of the electrolyte concentration decreases the anodizing voltage, but the volume expansion factor remains constant. Obtained dependence of the volume expansion factor of the porous alumina films on anodizing voltage exhibit a linear nature. For the 4% solution of oxalic acid all points of the temperature dependences are located on the same line. The approximation by the least-squares method has allowed the following equation for the k dependence on anodizing voltage in the 4% solution of oxalic acid to be established as:

$$k = 1.092 + 0.007 \times U \qquad (1)$$

The obtained dependences of anodic current density logarithm (lnj) on the inverse volume expansion factor of the porous alumina film (1/k) have a linear nature. All points obtained in 2%, 4% and 8 % solution of oxalic acid are located on the same line for the electrolyte temperature 20°C. Fig. 4 shows that each electrolyte temperature has its dependence of anodic current density logarithm on 1/k. The approximation by the least-squares method for various electrolyte temperatures has given the following equations:

$$T = 16°C,\ 1nj = 10.11 - 12.386 \times (1/k); \quad (2)$$

$$T = 18°C,\ 1nj = 10.28 - 12.39 \times (1/k);$$

$$T = 20°C,\ 1nj = 10.46 - 12.392 \times (1/k).$$

As it can be seen, the dependences of lnj on 1/k can be approximated by the linear function and a constancy of the slope for different electrolyte temperatures is observed.

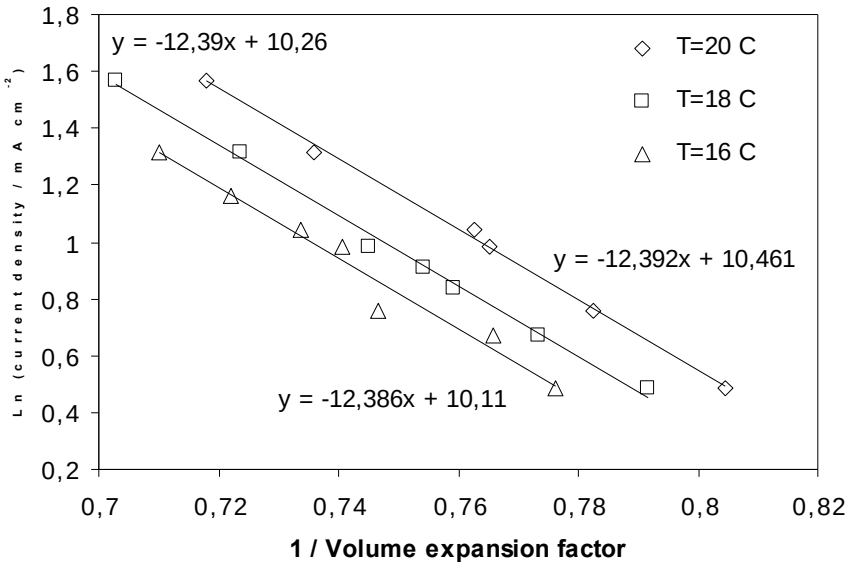

Fig. 4. Anodic current density logarithm vs. inverse volume expansion factor of the porous alumina film as a function of temperature (4 % solution of oxalic acid at the temperature of 16, 18 and 20°C).

3.2 Copper metallization

Figs. 5, 6 and 7 present the SEM images of copper-filled trenches in nanoporous alumina layer.

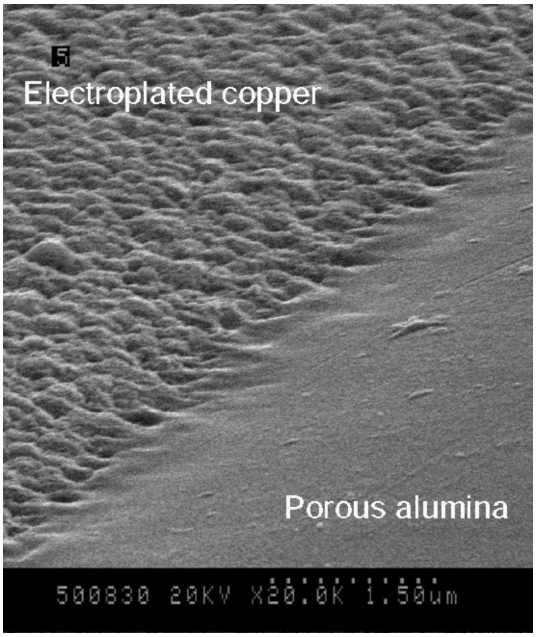

Fig. 5. A SEM image of electroplated copper-porous alumina interface

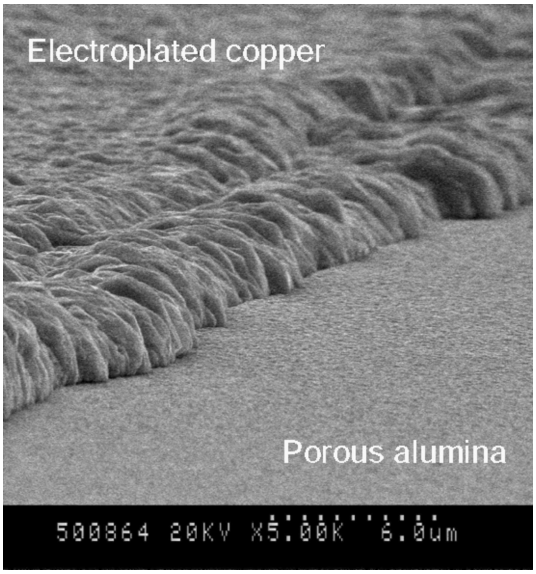

Fig. 6. A SEM image of electroplated copper-porous alumina interface

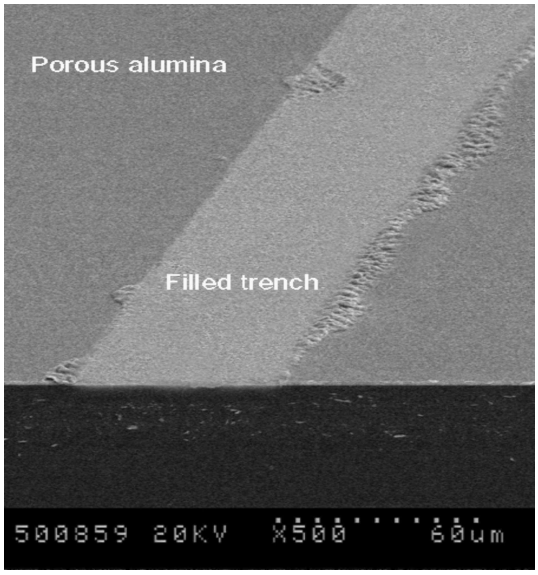

Fig. 7. A SEM image of Cu-filled trench

The possibility of integration porous anodizing of aluminum and copper electro-/electroless deposition techniques in the context of temperature sensor developing is presented.

4. Discussion

It is well known that the porous oxide film thickness is defined by the anodizing time and the current density according to the Faraday law. For example, for the steady-state anodic film formation at the constant anodic current density, the cell is of approximately constant unchanging dimension, and the barrier layer is maintained at the constant thickness beneath each pore [4]. The mechanism controlling the film formation is the balance between the film growth at the barrier layer and a field-assisted dissolution at the outer surface of the barrier layer.

Let us analyze the results of influence of the anodic current density, temperature and electrolyte concentration on the volume expansion factor of porous alumina films. As can be seen from Fig.3 and Fig.4, the increase of the electrolyte temperature from 16°C up to 20°C (4% solution of oxalic acid) for the anodic current density of 2.84 $mA \cdot cm^{-2}$ decreases the volume expansion factor of the porous alumina film from 1.36 down to 1.31. In this case the steady-state anodizing voltage decreases from 38.1V (16°C) down to 30.5V (20°C). It can be explained by the following reasons. There is a dependence of the field strength across the barrier layer on the anodic current density given by the high field conduction theory [17,18].

$$j_+ = A_+ \exp B_+ E \qquad (3)$$

where j_+ is the current density of cations of metal, A_+ is the temperature dependent coefficient, B_+ is the temperature independent coefficient associated with the ion process, E is the field strength.

In our experiments the total anodic current is approximately equal to the ion current. That is why in the equation (6) the value of the total anodic current can be used instead of the value of the ion current. This makes the analysis of the results much easier. With the increase of the electrolyte temperature, the value of the coefficient A_+ [10,15] increases resulting in the decrease of the electric field strength required to maintain the constant current density. It is well known that the barrier-layer thickness, cell

diameter and pore diameter of porous alumina films are directly proportional to the anodizing voltage [4]. Therefore, the barrier-layer thickness and the anodizing voltage should decrease down to the level corresponding to the lowest electric field strength. It is related with the increase of the field-assisted dissolution rate at the outer surface of the barrier layer when the electrolyte temperature increases. In this case, the decrease of anodizing voltage and, accordingly, cell dimensions of porous alumina results in the decrease of the volume expansion factor.

If anodic current density for the temperature of 16°C (Fig.3 and Fig.4) is chosen to be equal to 1.96 $mA \cdot cm^{-2}$, the volume expansion factor for alumina films is 1.31 and anodizing voltage is 31 V, then the same volume expansion factor during anodizing and the same anodizing voltage in the electrolyte at the temperature of 20°C and at the current density of 2.84 $mA \cdot cm^{-2}$ are observed. This fact indicates the interaction between the volume expansion factor and the anodizing voltage in the 4% solution of oxalic acid. Note that for porous alumina the interaction between the anodizing voltage and the electric field strength in the barrier layer also exists.

Influence of the current density on the volume expansion factor of porous alumina films. The increase in the anodic current density (that is the increase of the electric field strength) increases the volume expansion factor and the steady-state anodizing voltage. It confirms our conclusion about the interaction between the volume expansion during aluminum oxidation and the anodizing voltage.

Influence of the electrolyte concentration on the volume expansion factor of porous alumina films. At the constant anodic current density, the volume expansion factor does not depend on the electrolyte concentration. At the same time, at the anodic current density of 2.13 $mA \cdot cm^{-2}$ the decrease of the electrolyte concentration results in the increase of the anodizing voltage. This can be explained by the following. According to the equation (3), anodizing in electrolytes of various concentrations at the constant current density keeps the electric field strength in the barrier layers of porous oxides being constant. It is due to the fact that the processes at the metal/oxide interface control the ion current. The increase of the electrolyte concentration increases the field-assisted dissolution rate at the outer surface of the barrier layer of porous oxide. Therefore, to provide constant electric field strength in the oxide film, the barrier layer thickness and steady-state anodizing voltage should decrease.

Thus, the analysis of experimental results shows that the volume expansion factor of porous alumina films depends on the electric field strength in the barrier layer. The increase of the electric field strength in the barrier layer results in the increase of the volume expansion factor.

As it is known [19], the interpore distance increases linearly with the anodizing voltage and the relationship obtained from disordered porous anodic alumina also fits for periodic pore arrangements. Therefore, we can suggest that the established dependences for the volume expansion of Al during oxidation in the case of self-organized pore growth will also be systematical.

5. Conclusions

1. It was showed, that concentration variations of the electrolyte at the constant current density do not influence the volume expansion factor of porous alumina films. The decrease of the electrolyte temperature and the increase of the anodic current density result in its increase. This is explained by the fact that the volume expansion factor of porous alumina films (k) depends on the electric field strength in the barrier layer.

2. It was established, that the volume expansion factor as well as the cell dimensions is proportional to the anodizing voltage. The dependence of the volume expansion factor on anodizing voltage (U) has the linear nature. The volume expansion factor in the 4% solution of oxalic acid can be defined by the following equation:

$$k = 1.092 + 0.007 \times U$$

3. It was established, that the dependence of the logarithm of the ion current density on the inverse volume expansion factor of porous alumina has the linear nature. For dependences obtained at various temperatures and electrolyte concentrations, a constancy of the slope for different electrolyte temperatures is observed.

4. Present investigation demonstrated the control possibility of nanoporous alumina film characteristics which are strongly depend on parameters of anodization process of aluminum (anodization solution temperature and concentration, anodic current density and voltage) what is very important for thin copper film temperature sensors fabrication.

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